Impact of ageing on the leaching behavior of a calcareous sample excavated from Grand Paris Express construction sites and naturally contaminated in Molybdenum and Selenium

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Grand Paris Express (GPE) project

Modernization and enlargement of public transport facilities in Paris area

High Se and Mo mobility in GPE construction sites have been shown for different types of soils : calcareous, marly limestones, clayey…

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Excavation of more than **40M tons of earths** over a 10 years period

Parisian Basin geology often presents high natural concentration of **Molybdenum (Mo) and Selenium (Se)**

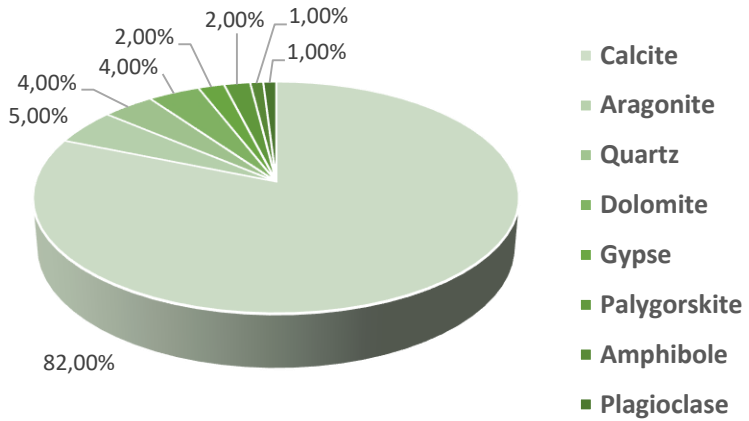
- ✓ Acceptation in Wastes Landfill of these earths is linked with their leaching behavior characterized by a standardized leaching test (NF EN 12457-2)
- ✓ Public companies are aiming to store excavated earths in Inert Wastes Landfill

Chemical Stabilization is investigated as a way to make a non-inert earth inert by modifying Trace Elements mobility

The long term efficacy of such treatment has to be proved !

Calcareous samples in GPE project

Complete characterization of raw samples has been carried out before any stabilization treatment



Pie chart representing mineral phases repartition obtained with XRD analysis

Parameter	Total content (ppm)
Mo	10,9
Se	2,76

Total amount of Mo and Se in the sample (Mineralization followed by ICP-MS analysis)

Parameter	Leachates concentration[a] (ppm)	Threshold value for Inert Wastes Landfill[b] (ppm)
As	0,013	0,5
Ba	0,30	20
TOC	14	500
Cl	18,3	800
F	9	10
Hg	0,001	0,01
Mo	**3,59**	**0,5**
Ni	0,009	0,4
SO_4	1178	6000
Sb	0,009	0,06
Se	**0,102**	**0,1**

- ✓ Sample mainly **composed of carbonates** (calcite, aragonite, dolomite)
- ✓ Low levels of TE do not prevent leaching concentration to **overpass acceptation criteria**
- ✓ Mo and Se are expected in association **with minor phases** (iron sulfides, iron and/or aluminum oxides…)

[a] *Mean of results obtained on triplicats according to the standardized leaching test NF EN 12457-2*

[b] *According to the European Decision 2003/33/CE*

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Stabilization long-term efficiency – Artificial ageing

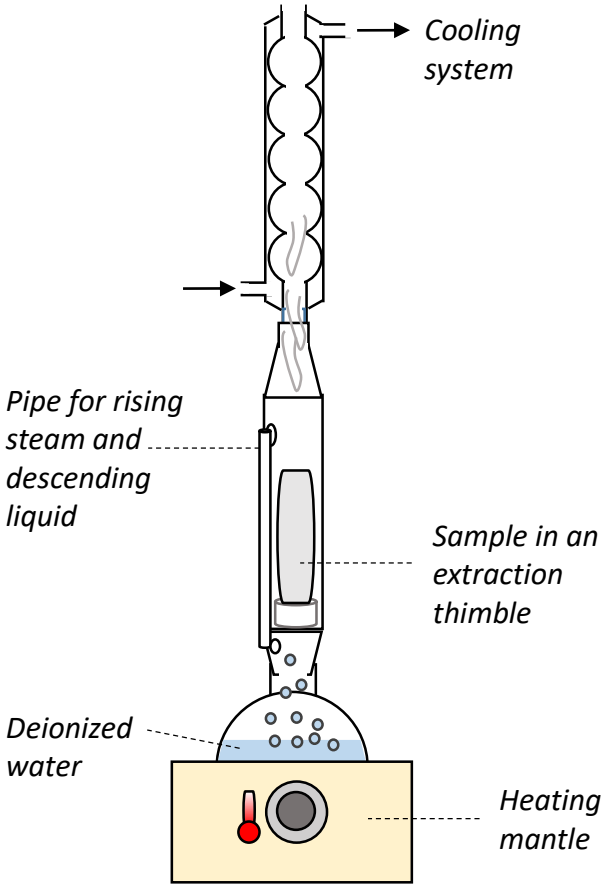
Soxhlet extractions have been carried out on samples before and after stabilization

Principle

The sample is placed on top of a round bottom flask filled with boiling water. A succession of immersion/flushing cycles will occur as the water would evaporate and condense in the cooling system. Flushing water are renewed every two days in the boiler and leachates are analyzed (ICP-MS) for Trace Elements (TE) concentrations.

Objective

- Favor the release of Trace Elements (high L/S ratio, leaching water renewal, pH and temperature modifications)
- Reach the highest leachable concentration and compare it between stabilized and non-stabilized samples
- See the role played by solid matrix alteration compared to the only action of water contact in classic leaching tests



Experimental conditions

Duration: 10 days

Liquid/Solid ratio for each cycle ≈ 2

Immersion/flushing cycle duration : 60 to 75 min

Cooling temperature : 5°C

Number of replicates for each sample : 3

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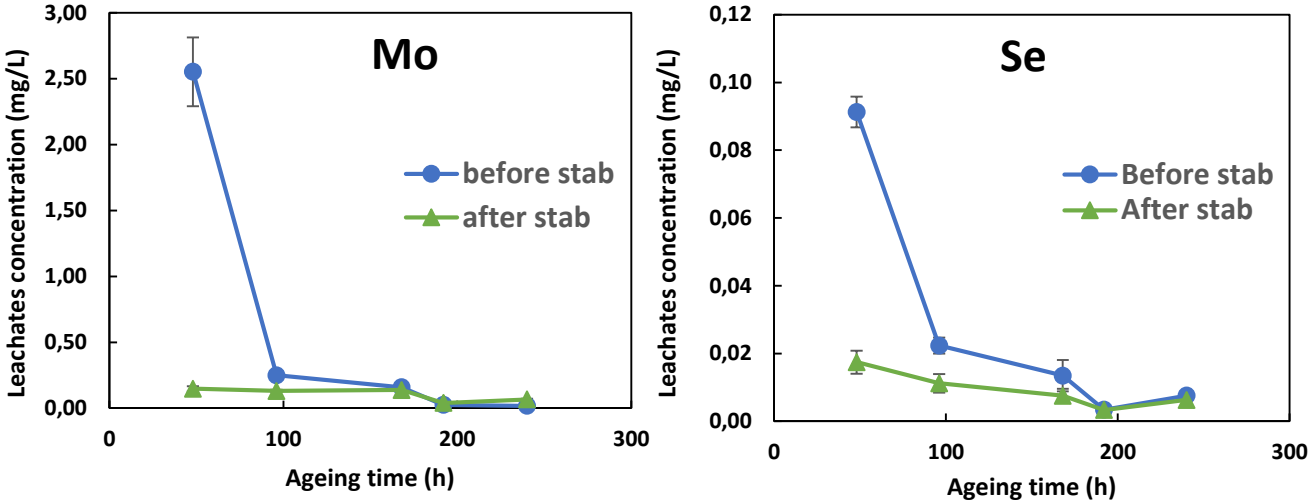
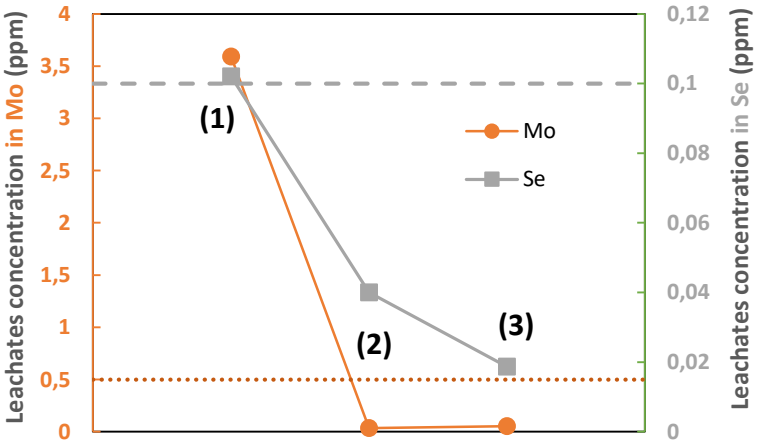
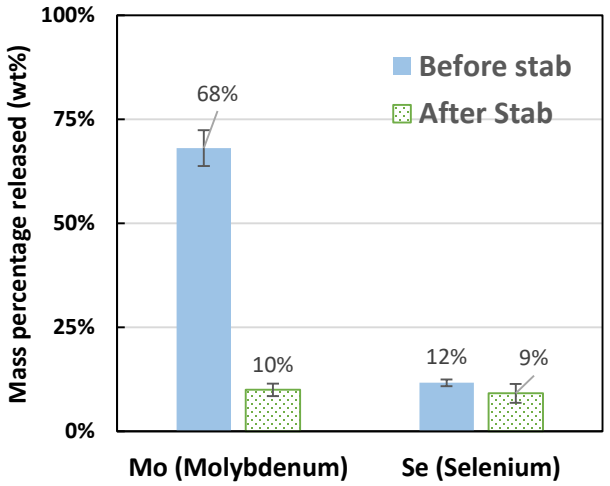
Which impact on TE mobility ?

Results are presented here for a calcareous sample with the best stabilizing agent (3 wt%)



Mo and Se concentration in leachates as a function of ageing duration





Mass percentage of TE released after 10 days of ageing

Mo and Se leachates concentration measured according to the standardized test NF EN 12457-2 carried out on samples before (1), after stabilization (2) and after ageing experiment (3) – Dashed and dotted lines represent threshold values for acceptance in Inert Wastes Landfill for Se and Mo respectively

Conclusions

For calcareous earths extracted in GPE construction sites

✓ Stabilization has shown a good ability to limit Mo and Se release at short (standardized leaching tests) and long (soxhlet extraction) term

✓ Retention of TE in the solid lattice seems to occur through strong phenomena since no further release are noticed in leaching tests carried out after ageing experiment

× The real role played by the stabilizing agent has not been yet completely understood and it will require further mineralogical and chemical analysis

For the other types of rocks extracted from GPE construction sites

✓ Stabilizing agents tested have been chosen after a complete characterization of samples representative from the GPE construction sites issues regarding TE release

⇨ TE speciation is different from one sample to another so that efficiency of stabilization as presented here has to be proved for each type of soil

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